Paper No. 41

“Fluoroelastomers and Modern Engine Fluids”

by Daniel L. Hertz, Jr., Andrew Farinella, and Hermann Bussem

Seals Eastern, Inc.

134 Pearl Street

Red Bank, NJ 07701

Presented at a meeting of the

Rubber Division, American Chemical Society

Dallas, Texas

April 4-6, 2000

(Augmented Aging Data 10/16/00)

FLUOROELASTOMERS AND MODERN ENGINE FLUIDS

Daniel L. Hertz, Jr., Hermann Bussem, and Andrew Farinella

Seals Eastern, Inc., 134 Pearl Street, Red Bank, NJ 07701

Phone: (732) 747-9200   Fax: (732) 747-3647

ABSTRACT

Two classes of fluoroelastomers, FKM and FEPM, are aged at 150°C in dry heat, ASTM reference engine oil and an organic acid based engine coolant. The test procedure, which uses unique component geometry, test jig and test vessel concept appears to offer a rapid (168 hours), reproducible measure of crosslink stability under real world conditions.

INTRODUCTION

Fluoroelastomers with their associated high temperature resistance are increasingly utilized in both spark ignition (SI) and diesel (CI or compression ignition) engines. Routine operating temperatures of 150°C (302° F) and higher for both coolants and lubricants indicate more extensive use of this class of elastomer. This paper reviews fluoroelastomers of two categories- FKM and FEPM- in both an engine coolant and a hydrocarbon lubricant. Initial evaluation was performed by monitoring long-term compressive stress relaxation (CSR) at 150°C (302° F). Data is reported for the first 1008 hours; testing is ongoing.

EXPERIMENTAL

The CSR test specimen is essentially a rubber ball (sphere) of 6.35 mm (0.25 in) diameter with a molded thin-walled centering ring (see Figure 1). The spherical shape offers several advantages, e.g. maximum volume with minimum surface area, contact area and contact pressure similar to an o-ring, deformable in essentially a linear section of a stress-strain plot (see Figure 2).

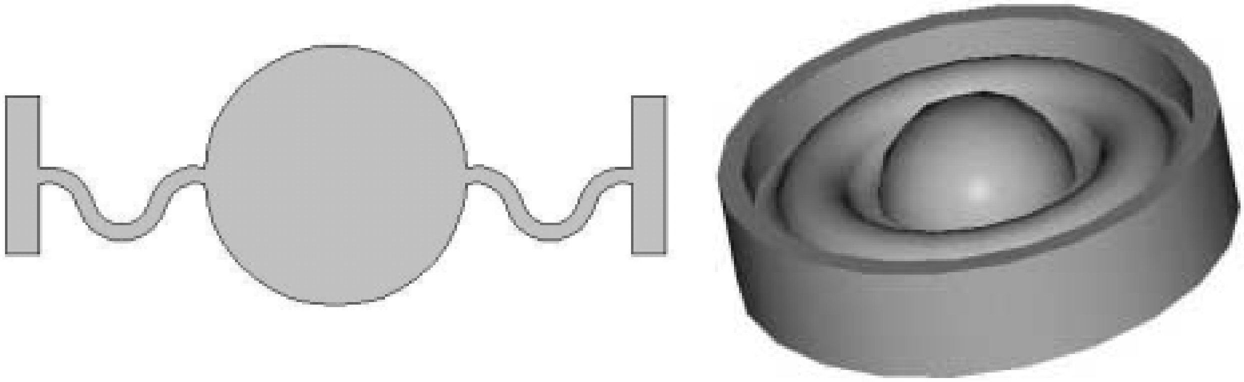

FIG. 1. —Spherical Test Specimen (Cross Section and Isometric)

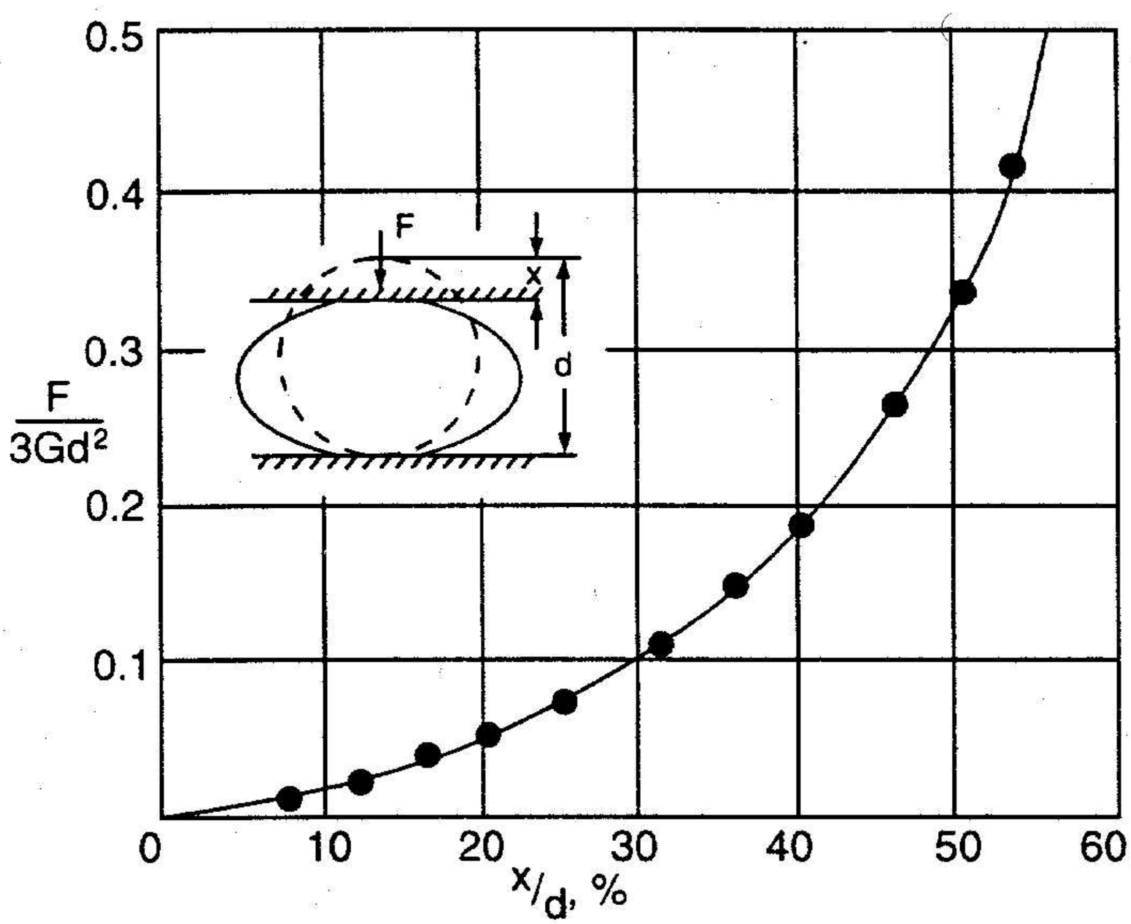

FIG. 2. — Compression of a Rubber Sphere[1]

(Reproduced with permission)

The test jig (Figure 3) can be economically produced in large quantities for use in environmental chambers, ovens and pressure vessels. The test specimen is centralized in the test jig by the locating ring; when compressed by tightening the stripper bolt screws, the deformation is 25%. The spherical seal is now sealing the 0.8 mm (0.03 in) pressure port.

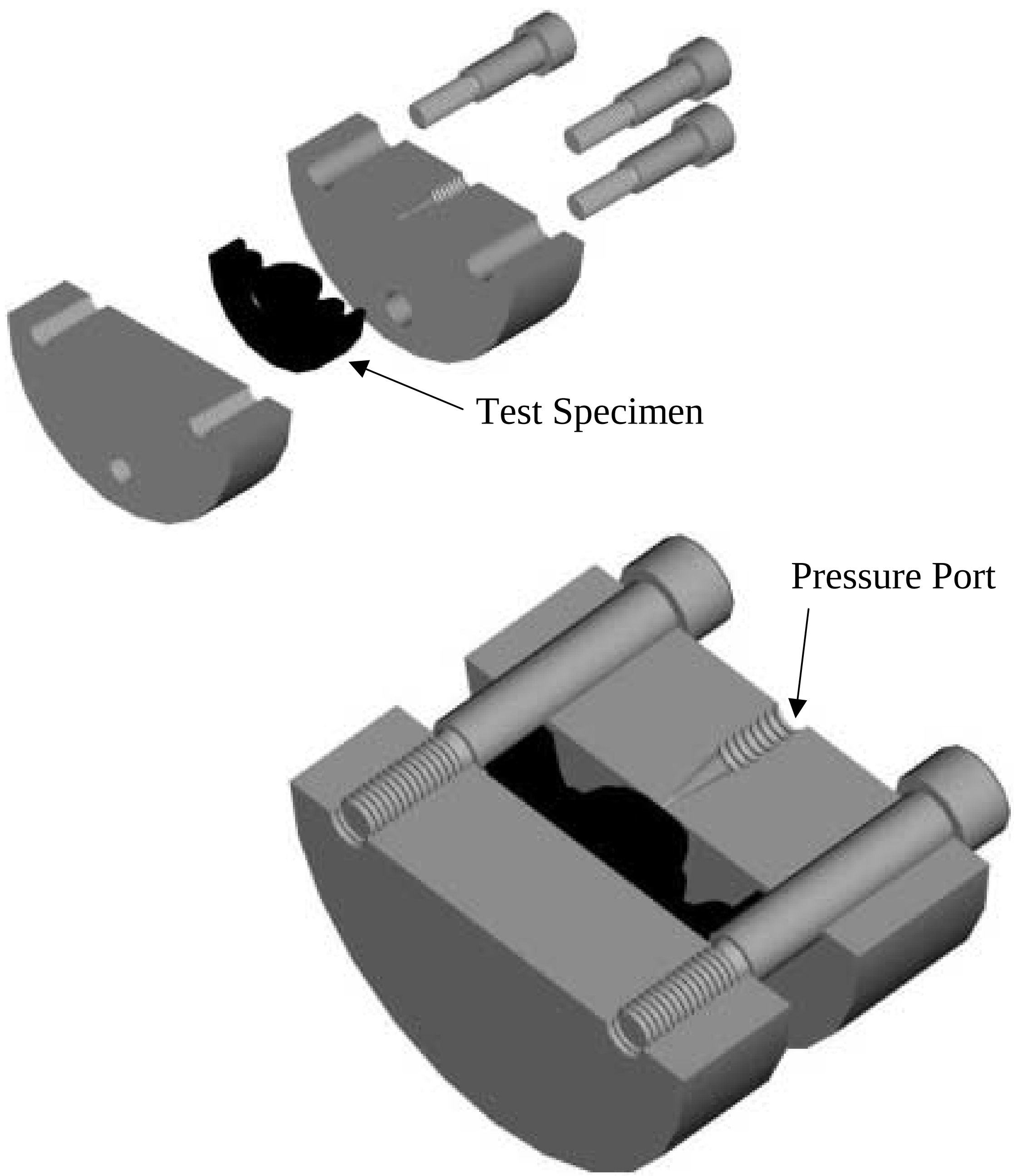

FIG. 3. — Test Fixture Assembly

The pressure test fixture (See also Figure 3) uses any convenient source of gas pressure (typically 11 MPa or 1,600 PSI). By having a gage and/or pressure transducer between the test jig and pressure source, when the line is charged and the pressure source isolated, the test jig/CSR specimen will relieve the pressure until the rubber ball contact stress is equivalent to the system pressure. Equilibrium is normally achieved within 120 seconds. The pressure value is recorded and the fixture removed for additional aging if desired. The size is sufficiently compact as to allow a multiple number of jigs to be incorporated in an environmental test chamber so both high and low temperature sealability can be determined. The use of dissimilar metals in the fluid aging vessel (Figure 4) will also introduce legitimate electrochemical effects.

FIG. 4. — Fluid Aging Vessel

Test fluids were selected to represent reasonable current practice, e.g. ASTM reference oil TMC 1006 represents SAE 5W-30 engine oil and is the recommended test fluid in D471-98, identified as service liquid 105 (SF-105). Engine coolants are currently undergoing a globalization of environmentally acceptable formulations. The organic acid technology as represented by Texaco's "Extended Life Coolant" (TELC) was selected to be representative of this group.

Elastomers: FKM, a dipolymer of vinylidene fluoride/hexafluoropropylene was compounded in accordance with AMS-R-83248. FEPM, a dipolymer of tetrafluoroethylene/propylene was compounded using proprietary in-house technology.

RESULTS

Figures 5, 6 and 7 illustrate compressive stress decay graphically. SF-105 (Figure 5) is particularly aggressive on the FKM sample; this would be the result of the nucleophilic stabilizers dehydrofluorinating VF_2 sites with subsequent polymer cleavage. The FKM testing was discontinued after 336 hours. FEPM reaches equilibrium after the same time period (7.5% drop in compressive stress between 500 and 3,000 hours).

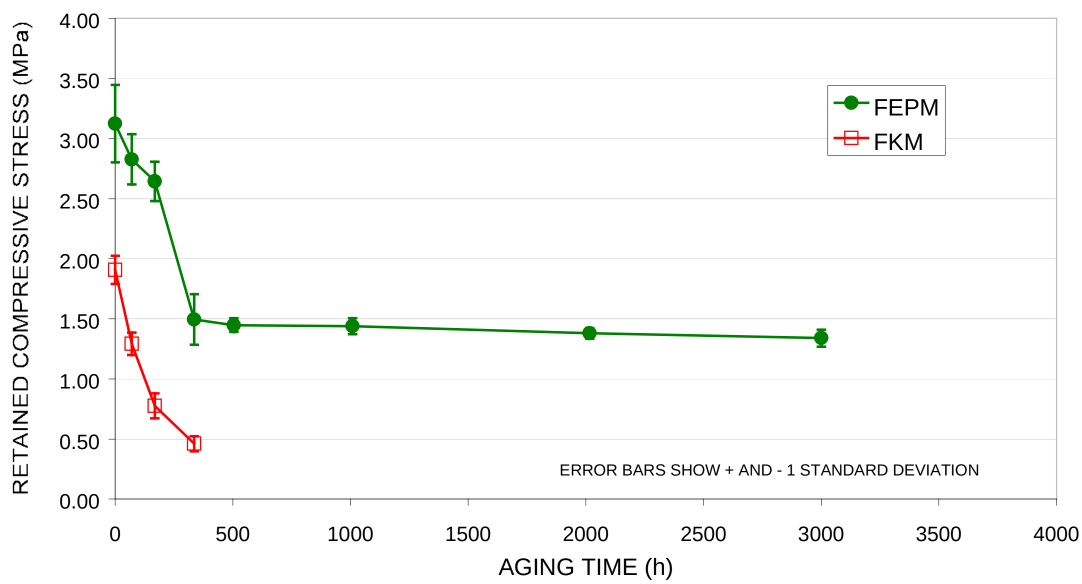

FIG. 5. — Retained Compressive Stress vs. Aging Time

SF-105 Fluid at 150°C

TELC (Figure 6) is even more aggressive on FKM with testing discontinued after 168 hours. The rapid stress decay is probably due to hydrolysis of the crosslinks. FEPM is beginning to stabilize after 504 hours and remains at a virtual plateau through 4,000 hours of aging (2.6% drop in compressive stress between 500 and 4,000 hours).

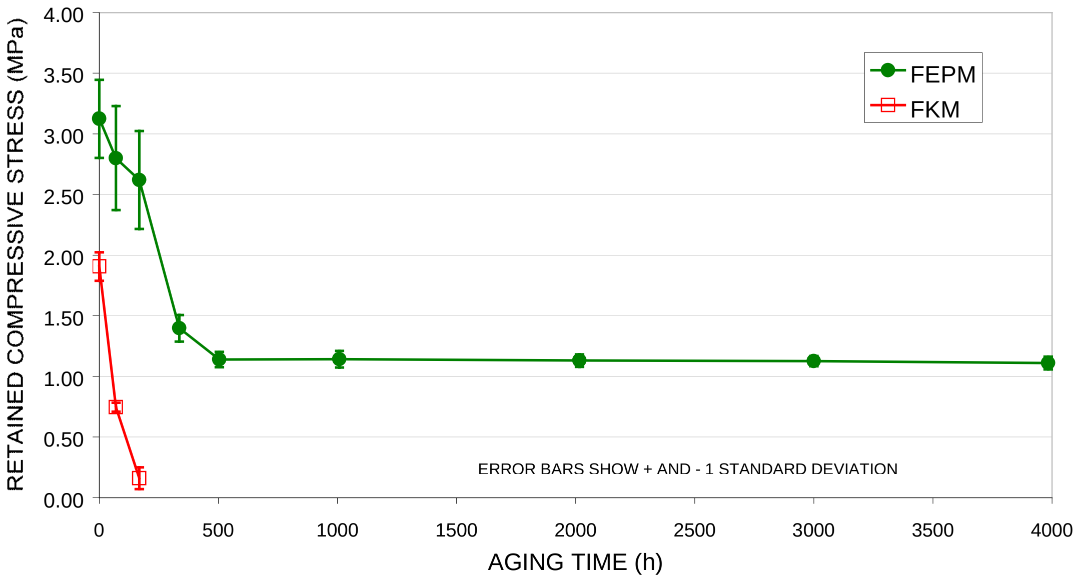

FIG. 6. — Retained Compressive Stress vs. Aging Time

TELC Fluid at 150°C

Dry heat (Figure 7) is aggressive on the FKM, although the rapid decay is not predictable from the excellent compression set resistance reported by FKM suppliers. Testing of FKM was discontinued after 168 hours while the FEPM reaches a plateau after approximately 500 hours and remains nearly flat through 4,000 hours (6.3% drop in compressive stress between 500 and 4,000 hours).

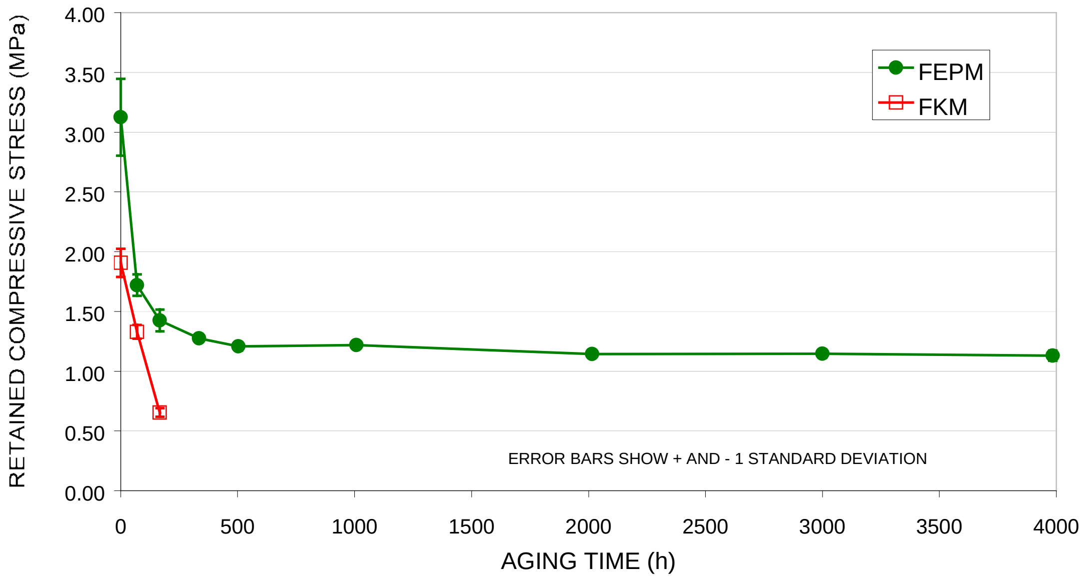

FIG. 7. — Retained Compressive Stress vs. Aging Time

Dry Heat at 150°C

DISCUSSION

FKM elastomers have had great success over many years in critical applications. However, this test program was done using fluids we should correctly refer to as aqueous electrolytes (TELC) and non-aqueous electrolytes (SF-105). In both of these liquids we have a strong nucleophilic (electron donor) presence. To preserve the integrity of the test program, both materials (FKM and FEPM) were tested for 70 hours in spectrophotometer grade "Nujol," a pure white paraffin oil (Figure 8). Note that while FKM was essentially flat, FEPM showed the typical initial rapid decline in retained stress.

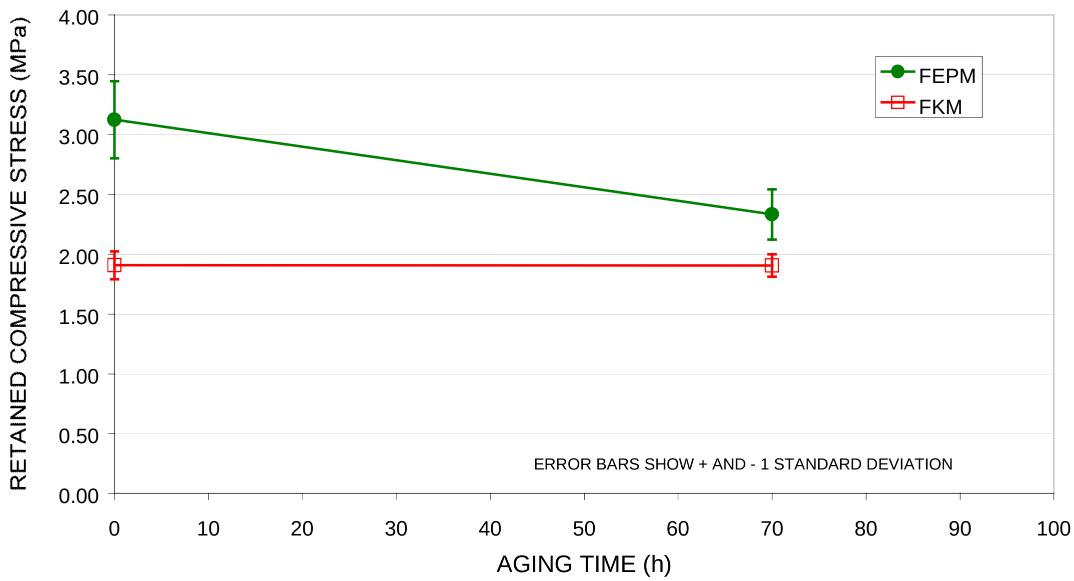

FIG. 8. — Retained Compressive Stress vs. Aging Time

Nujol at 150°C

This phenomenon is a function of our particular compounding approach and is essentially the same as the "Mullins Effect" common to engineered dynamic rubber components.

CONCLUSIONS

The proposed test geometry appears to offer a rapid screening test for better understanding of the compressive stress relaxation behavior of various materials when subjected to virtually any desired service conditions (aging time, fluid and temperature).

SUMMARY

Compressive stress relaxation is essentially the process of "dying" a mechanically loaded elastomeric component undergoes. Having knowledge of the rate and an actual value (particularly for seals) of retained stress is very helpful. Modifications of the test apparatus should allow development of actual low-temperature sealing values.

ACKNOWLEDGEMENT

The authors would like to thank David W. Arnwine, who not only did most of the actual testing but also developed techniques and processes which greatly improved the repeatability of multiple (4) specimens for each data point.

REFERENCES

1. "Engineering Design with Natural Rubber." *NR Technical Bulletin.* The Malaysian Rubber Producers' Research Association. ISSN 0956-3856.